

Hydrogen bonding in nitroaniline analogues: a three-dimensional framework in 2-amino-6-nitro-1,3-benzothiazole

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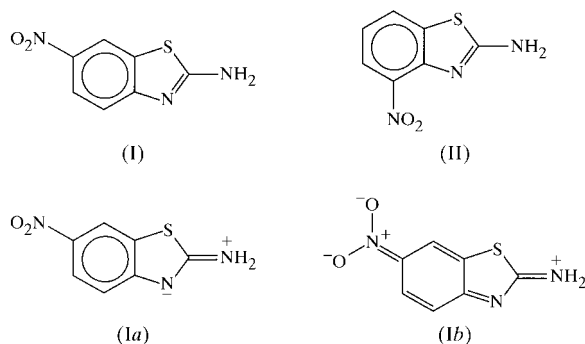
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In the title compound, C₇H₅N₃O₂S, the molecules are linked into a three-dimensional framework by a combination of a three-centre N—H···(O)₂ hydrogen bond, and two-centre N—H···N and C—H···O hydrogen bonds.

Comment

In nitroanilines where the amino and nitro substituents are remote from one another such that intramolecular hydrogen-bond formation is precluded, the molecules generally act as double donors and double acceptors of hydrogen bonds; the resulting supramolecular structures can be either two-dimensional (Ploug-Sørensen & Andersen, 1986; Tonogaki *et al.*, 1993; Ellena *et al.*, 1999; Cannon *et al.*, 2001) or three-dimensional (Ferguson *et al.*, 2001). The effect of introducing an excess of hydrogen-bond acceptors, as in 3,5-dinitroaniline



(Glidewell *et al.*, 2001), can be unexpected; in this compound, not all of the N—H bonds are engaged in hydrogen bonding, despite the excess of acceptors over donors. Pursuing this theme, we have now investigated the molecular and supramolecular structure of 2-amino-6-nitro-1,3-benzothiazole, (I), where the ring N atom provides an additional hydrogen-bond acceptor site, so giving an excess of acceptors over donors.

Molecules of (I) (Fig. 1) are linked by N—H···O, N—H···N and C—H···O hydrogen bonds (Table 2) into a three-dimensional framework, which is reinforced by aromatic π – π -stacking interactions; the framework structure can readily be analysed in terms of the low-dimensional motifs generated by the individual hydrogen bonds in turn.

The amino N2 atom acts as hydrogen-bond donor, *via* H22, in a nearly planar three-centre system where the two acceptors are O71 atoms in two different molecules (Table 2). Atom N2 at (x, y, z) acts as donor to O71 at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, so producing a C(9) chain running parallel to the [010] direction

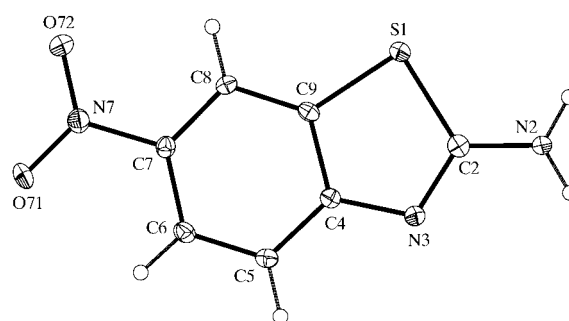


Figure 1
The molecular structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

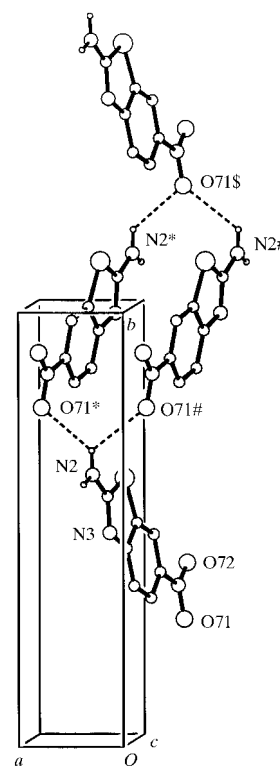


Figure 2
Part of the crystal structure of (I) showing the formation of an $R_3^2(20)$ ring in the (001) sheet by a three-centre N—H···(O)₂ hydrogen bond. H atoms bonded to C atoms have been omitted for clarity. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, $(-\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(x, 1 + y, z)$, respectively.

and generated by the 2_1 axis along $(\frac{1}{4}, y, \frac{3}{4})$; at the same time, N2 at (x, y, z) also acts as donor to O71 at $(-\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, producing a similar $C(9)$ spiral chain around the 2_1 axis along $(-\frac{1}{4}, y, \frac{3}{4})$. The combination of these two one-dimensional motifs generates a sheet parallel to (001) in the form of a (4,4)-net (Batten & Robson, 1998) built from a single type of $R_3^2(20)$ ring (Fig. 2). This sheet is reinforced by aromatic π - π -stacking interactions; in molecules related by translation along the [100] direction, the interplanar spacing is *ca* 3.38 Å and there is π - π overlap between the carbocyclic ring of the molecule at (x, y, z) with the heterocyclic ring of the molecule at $(-1 + x, y, z)$, with a centroid offset of *ca* 1.24 Å (Fig. 2); propagation of this interaction by translation gives a sheared-stack motif.

There are two (001) sheets passing through each unit cell, one in the domain $-0.02 < z < 0.52$ and the other in the domain $0.48 < z < 1.02$, and these sheets are linked into a three-dimensional framework by almost linear N—H...N hydrogen bonds, whose effect is reinforced by C—H...O hydrogen bonds (Table 2). The amino N2 atom at (x, y, z) lies in the domain $0.48 < z < 1.02$ and acts as hydrogen-bond donor, *via* H21, to the thiazole N3 atom in the molecule at $(1 - x, 1 - y, 1 - z)$, which lies in the domain $-0.02 < z < 0.48$; N2 at $(1 - x, 1 - y, 1 - z)$, in turn, acts as donor to N3 at (x, y, z) , so generating a centrosymmetric $R_2^2(8)$ motif (Fig. 3). Similarly, N2 at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, which also lies in the domain $0.48 < z < 1.02$, acts as donor to N3 at $(-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, which lies in the domain $0.98 < z < 1.52$. In this manner, each (001) sheet is linked to its two immediate neighbours, so generating a continuous three-dimensional array.

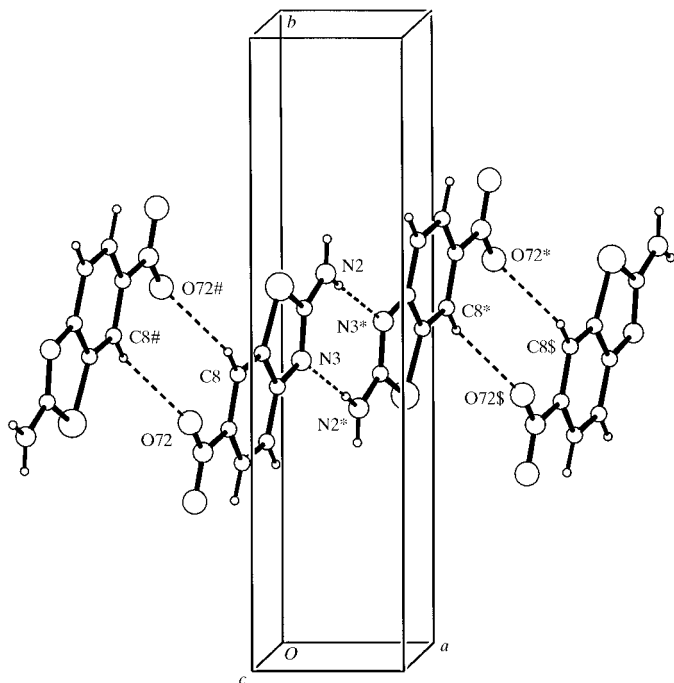


Figure 3
Part of the crystal structure of (I) showing a $[201]$ chain of alternating $R_2^2(8)$ and $R_2^2(10)$ rings which link adjacent (001) sheets. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(-1 - x, 1 - y, 2 - z)$ and $(2 + x, y, -1 + z)$, respectively.

Atom C8 at (x, y, z) , in the domain $0.48 < z < 1.02$, acts as hydrogen-bond donor to the nitro O72 atom at $(-1 - x, 1 - y, 2 - z)$, which is in the domain $-0.02 < z < 0.52$. In so doing, it generates a centrosymmetric $R_2^2(10)$ motif, and the propagation of this motif of paired C—H...O hydrogen bonds again serves to link each (001) sheet to each of its neighbours. The combination of these two cyclic motifs generates a $C_2^2(14)[R_2^2(8)][R_2^2(10)]$ chain of rings running parallel to the $[\bar{2}01]$ direction (Fig. 3).

In the isomeric 2-amino-4-nitrobenzothiazole, (II) [Cambridge Structural Database (CSD; Allen & Kennard, 1993) refcode ZUHVUT (Lokaj *et al.*, 1996)], the hydrogen bonding

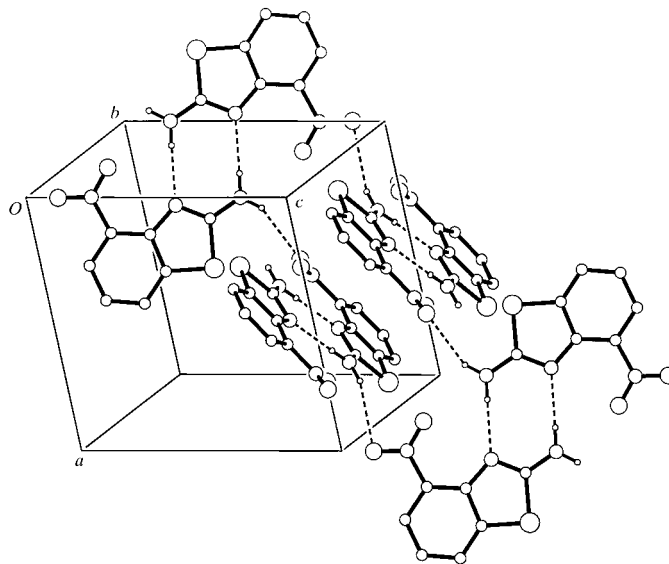


Figure 4
Part of the crystal structure of ZUHVUT (Lokaj *et al.*, 1996) showing the formation of a $(10\bar{1})$ sheet built from $R_2^2(8)$ and $R_6^0(32)$ rings. H atoms bonded to C atoms have been omitted for clarity.

links the molecules into $(10\bar{1})$ sheets (Fig. 4) rather than into a three-dimensional array. A combination of N—H...O and N—H...N hydrogen bonds generates a checkerboard array of $R_2^2(8)$ and $R_6^0(32)$ rings; the resulting net is of (4,4)-type (Batten & Robson, 1998) if the dimeric units produced by the $R_2^2(8)$ motif are regarded as the nodes of this net.

Within the molecule of (I), the C2—N2 and C2—N3 distances are very similar (Table 1); both the exocyclic C—N bonds are short for their types (Allen *et al.*, 1987) and there is evidence of quinonoid-type bond fixation within the aryl ring, indicating that forms (Ia) and (Ib) both contribute to the overall structure.

Experimental

A sample of (I) was obtained from Aldrich. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol.

Crystal data

$C_7H_5N_3O_2S$	$D_x = 1.649 \text{ Mg m}^{-3}$
$M_r = 195.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 1785 reflections
$a = 3.7715 (2) \text{ \AA}$	$\theta = 3.0\text{--}27.5^\circ$
$b = 15.6399 (8) \text{ \AA}$	$\mu = 0.38 \text{ mm}^{-1}$
$c = 13.3484 (9) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 93.252 (2)^\circ$	Needle, yellow
$V = 786.10 (8) \text{ \AA}^3$	$0.48 \times 0.10 \times 0.02 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	1785 independent reflections
φ scans, and ω scans with κ offsets	1252 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>DENZO-SMN</i> ; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.061$
$T_{\text{min}} = 0.837$, $T_{\text{max}} = 0.990$	$\theta_{\text{max}} = 27.5^\circ$
8740 measured reflections	$h = -4 \rightarrow 4$
	$k = -20 \rightarrow 20$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2]$
$wR(F^2) = 0.108$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1785 reflections	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
118 parameters	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

S1—C2	1.758 (2)	C8—C9	1.378 (3)
C2—N3	1.321 (3)	C9—S1	1.746 (2)
N3—C4	1.376 (3)	C4—C9	1.419 (3)
C4—C5	1.397 (3)	C2—N2	1.331 (3)
C5—C6	1.378 (3)	C7—N7	1.455 (3)
C6—C7	1.394 (3)	N7—O71	1.243 (2)
C7—C8	1.386 (3)	N7—O72	1.228 (2)
C6—C7—N7—O71	1.0 (3)	C6—C7—N7—O72	-178.61 (18)

Compound (I) crystallized in the monoclinic system; space group $P2_1/n$ was assigned from the systematic absences. H atoms were treated as riding with a C—H distance of 0.95 \AA and an N—H distance of 0.88 \AA .

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek,

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H21 \cdots N3 ⁱ	0.88	2.05	2.912 (2)	165
N2—H22 \cdots O71 ⁱⁱ	0.88	2.54	3.119 (2)	124
N2—H22 \cdots O71 ⁱⁱⁱ	0.88	2.41	3.051 (2)	130
C8—H8 \cdots O72 ^{iv}	0.95	2.53	3.381 (3)	149

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $-1-x, 1-y, 2-z$.

2001); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton. The authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1076). Services for accessing these data are described at the back of the journal.

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